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# *IN SITU* BIAXIAL TEXTURE ANALYSIS OF MGO FILMS DURING GROWTH ON AMORPHOUS SUBSTRATES BY ION BEAM-ASSISTED DEPOSITION

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# *IN SITU* BIAXIAL TEXTURE ANALYSIS OF MGO FILMS DURING GROWTH ON AMORPHOUS SUBSTRATES BY ION BEAM-ASSISTED DEPOSITION

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## ABSTRACT

We used a previously reported kinematical electron scattering model[1] to develop a RHEED based method for performing quantitative analysis of mosaic polycrystalline thin film in-plane and out-of-plain grain orientation distributions. RHEED based biaxial texture measurements are compared to X-Ray and transmission electron microscopy measurements to establish the validity of the RHEED analysis method. *In situ* RHEED analysis reveals that the out of plane orientation distribution starts out very broad, and then decreases during IBAD MgO growth. Other results included evidence that the in-plane orientation distribution narrows, the grain size increases, and the film roughens as film thickness increases during IBAD MgO growth. Homoepitaxy of MgO improves the biaxial texture of the IBAD layer, making X-ray measurements of IBAD films with an additional homoepitaxial layer not quantitatively representative of the IBAD layer. Systematic offsets between RHEED analysis and X-ray measurements of biaxial texture, coupled with evidence that biaxial texture improves with increasing film thickness, indicate that RHEED is a superior technique for probing surface biaxial texture.

## INTRODUCTION

Biaxially textured MgO is technologically interesting since it provides a suitable path for silicon integration of single crystal like films for many important perovskite materials. This is accomplished by using ion beam assisted deposition (IBAD) to create biaxially textured films (polycrystalline films with a preferred in-plane and out-of-plane grain orientation) on amorphous substrates. Film functionality often depends on both the out of plane grain orientation distribution (FWHM is designated as $\Delta\omega$) and in-plane grain orientation distribution (designated as $\Delta\phi$). Some highly aligned biaxially textured oxide materials can exhibit similar functionality to single crystalline films. For example, biaxially textured superconductors like $YBa_2Cu_3O_{7-x}$ have been reported to have critical current densities approaching those of single crystalline films, while randomly oriented polycrystalline films exhibit much lower critical current densities. Biaxially textured piezoelectric films with $90^o$ domain rotations are also expected to have flexing characteristics similar to those of single crystalline piezoelectric films, while randomly oriented polycrystalline piezoelectric films experience significant degradation of translational range of motion. Incorporation of biaxially textured piezoelectric films with silicon integrated circuits would enable new types of actuators for micro electrical mechanical systems (MEMs). Previous work has shown that piezoelectric materials like $Pb(Zr,Ti)O_3$ and $BaTiO_3$ can be deposited heteroepitaxially onto single crystal MgO (001)[2,3] and even Si (001)[4]. However, conventional silicon integrated circuit processing employs extensive hydrogen passivation, which degrades ferroelectrics like $Pb(Zr,Ti)O_3$ and $BaTiO_3$. It is therefore desirable to monolithically integrate piezoelectric materials following integrated circuit fabrication. Wang et al. demonstrated that IBAD MgO grown on amorphous

$Si_3N_4$ develops narrow biaxial texture in films only 11 nm thick[5]. By eliminating the requirement for a pre-existing heteroepitaxial template, IBAD provides an opportunity to incorporate piezoelectric materials on top of amorphous dielectric films in silicon integrated circuits during the backend processing.

The performance of piezoelectric MEMs is likely to depend on the biaxial texture inherited from the MgO substrate. Previous efforts to optimize the biaxial texture of IBAD MgO have been impeded by the *ex situ* nature of conventional biaxial texture analysis techniques (transmission electron microscopy - TEM or X-ray diffraction). Because the biaxial texture develops within 11 nm of growth, X-ray diffraction cannot resolve crystallographic texture unless the X-ray source has synchrotron brightness. For these same reasons, the IBAD biaxial texturing mechanisms are also poorly understood. To circumvent these obstacles we have developed a reflection high-energy electron diffraction (RHEED) based method for quantitative *in situ* biaxial texture analysis of MgO. Because RHEED is sensitive to films as thin as 30 angstroms thick we expect to have the capability of analyzing the biaxial texture development during grain growth, film coalescence, and film growth. This analysis should lead to greater understanding of IBAD MgO biaxial texture development and how to optimize the MgO biaxial texture.

## EXPERIMENTAL APPROACH AND MODEL-BASED ANALYSIS

Our RHEED based biaxial texture analysis employs a previously reported kinematical electron scattering calculation[1]. These calculations predict that spot shapes are sensitive to the film microstructure. Diffraction spot width and height are inversely proportional to the grain size and electron penetration depth, respectively. The width of the diffraction spot in the direction perpendicular to the location of the through spot is directly proportional to the out-of-plane grain orientation distribution ($\Delta\omega$). We therefore characterize RHEED patterns (whether calculated using a computer simulation or from an experiment) by cutting across the diffraction spots along the previously mentioned directions and measuring the FWHM of these cuts, as shown in Figure 1. Several spots can be analyzed simultaneously, and then compared to calculated RHEED patterns using a lookup table. The film grain size, electron penetration depth, and $\Delta\omega$ are determined by searching the lookup tables for the simulated film values that yield the smallest error between the calculations and experiment. This technique is not very sensitive to the film in-plane orientation distribution, which is measured using RHEED in-plane rocking curves, as previously described[1].

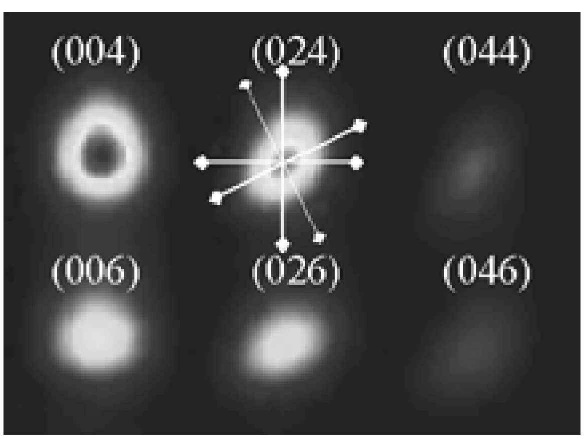


Figure 1: RHEED image of IBAD MgO. The relevant diffraction spots are indexed and the single image analysis diffraction spot measurement directions are shown on the (024) diffraction spot.

To experimentally measure in-plane orientation distribution ($\Delta\phi$), the FWHM of several in-plane rocking curves from different diffraction spots, are measured simultaneously and compared to the FWHM of calculated in-plane rocking curves using a lookup table. The in-plane orientation distribution is determined by searching the lookup table for the simulation that has RHEED in-plane rocking curves that most closely match the experimental rocking curves for all spots. The FWHM of the in-plane rocking curves are highly correlated with the in-plane orientation distribution, however, the rocking curve FWHM is also convoluted with the grain size and out-of-plane orientation distribution. Therefore, to accurately measure in-plane orientation distribution using rocking curves, the grain size and out-of-plane orientation distribution is first measured using single image analysis as described above. The subsequent comparisons between the experimental and simulated FWHM of the in-plane rocking curves in the lookup tables are restricted to simulations with the previously measured grain size and electron penetration depth.

Experimental RHEED in-plane rocking curves and single image analyses were performed on eight IBAD MgO samples grown at Los Alamos National Laboratories. A single crystal of MgO was also analyzed for reference. The IBAD MgO films were ~ 11nm thick, deposited on amorphous $Si_3N_4$/Si (001). RHEED measurements were done at 25 kV and 2.6 degrees incidence angle, unless otherwise specified. Bragg spots along the (00), (02), and (04) Bragg rods, as shown in Figure 1, were used in the RHEED analysis. In-plane orientation distributions were measured using either grazing incidence X-ray diffraction or TEM. Some samples were evaluated using both TEM and X-Ray $\theta-2\theta$ scans to determine the average grain size, while the out-of-plane orientation distributions were evaluated using X-ray rocking curves. Because the IBAD MgO layer is only 11 nm thick, X-ray scattering was performed using synchrotron radiation for the out-of-plane rocking curves and $\theta-2\theta$ scans.

In order to investigate biaxial texture development during IBAD MgO growth we performed real time RHEED measurements. Ion irradiation during MgO growth was performed with 750 eV Ar+ ions at $45^{o}$ incidence angle. MgO was simultaneously deposited, using e-beam evaporation, at a rate of 2.1 Å/s, as measured by a quartz crystal oscillator. In some cases, epitaxial MgO was deposited without Ar+ irradiation on top of the ~11 nm thick IBAD MgO film at $600^{o}$ C and 1.0 Å/s. RHEED images were acquired using a 16 bit, 1024x1024 pixel CCD camera. Because of the high resolution and dynamic range required for this experiment, images could be acquired every 5 seconds, which corresponds to about one RHEED image per monolayer of film growth. Some growth experiments were performed with RHEED energies of 15kV and $3.4^{o}$ incidence.

## RESULTS

Measurements of out-of-plane orientation distribution ($\Delta\omega$) and grain size (L) using TEM, X-ray diffraction, and RHEED are summarized in Table 1. Rocking curve and single image analyses both generally yield the correct relative grain sizes and out-of-plane orientation distributions, however, the rocking curve measurements differ from those measured with TEM and X-ray diffraction. This is attributed to the convolution of these parameters with the in-plane orientation distribution. Single image analysis is predicted by the simulation to be independent of the in-plane orientation distribution and also yields results that are very similar

Table 1: Comparison of measurements made for grain size and out of plane orientation distribution ($\Delta\omega$) using X-ray/TEM and RHEED methods

| | Grain Size (nm) | | | Out of Plane Orientation Distribution (degrees) | | |
|---|---|---|---|---|---|---|
| Sample | X-Ray/TEM | Single Image | In-Plane | X-Ray/TEM | Single Image | In-Plane |
| M306 | 6.6 | 9.5 | 33.9 | 7.1 | 5.6 | 8 |
| M307 | 6.2 | 9.2 | 28.2 | 6.4 | 6.2 | 8 |
| M312 | 7.0 | 11.0 | 34.3 | 6.0 | 5.0 | 9 |

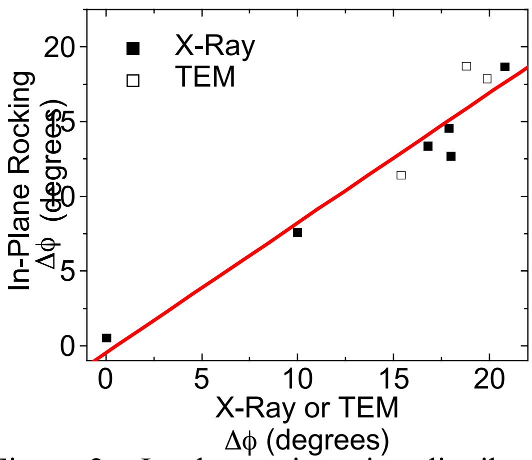

Figure 2: In-plane orientation distribution ($\Delta\phi$) FWHM as measured by RHEED analysis vs. $\Delta\phi$ measured using either X-ray diffraction or TEM

to the values from TEM and X-ray measurements. For this reason, only values for grain size and out-of-plane orientation distribution measured by single image analysis are used in the in-plane rocking curve lookup tables.

Figure 2 is a scatter plot of in-plane orientation distributions measured by RHEED and also by TEM or X-ray scattering. The data are well represented by a linear fit. However, there is a systematic offset between the RHEED analysis results and the TEM and X-ray diffraction measurements. X-ray scattering probes the entire film thickness rather than the surface, so it measures the in-plane orientation distribution averaged throughout the film thickness. RHEED is much more surface sensitive and therefore measures the in-plane orientation of only the topmost film layers. During IBAD MgO growth, the in-plane orientation distribution narrows with increased film thickness. Therefore it is reasonable to expect that RHEED would measure narrower in-plane orientation distributions than X-ray diffraction. The results are analogous for RHEED measurements of out-of-plane orientation distributions and grain size. Out-of-plane orientation distributions narrow with increased film thickness and grain sizes increase. The surface sensitivity of RHEED versus the film average measurements of X-ray diffraction explain why RHEED measurements are narrower and larger for out-of-plane orientation distributions and grain sizes, respectively (see Table 1). In general, RHEED based microstructure analyses yield more accurate estimates of surface biaxial textures than does X-ray diffraction.

Using biaxial texture RHEED analysis we have measured film grain size, in-plane orientation distribution ($\Delta\phi$)), out-of-plane orientation distribution ($\Delta\omega$)), and roughness during IBAD MgO growth and subsequent MgO homoepitaxy. Figure 3 summarizes the measured grain size, surface roughness, $\Delta\omega$, and $\Delta\phi$ as a function of approximate film thickness. Measurements below 3 nm film thicknesses are not reported because the RHEED pattern was irresolvable. These film thicknesses are estimated based on previous observations by C.P. Wang that MgO diffraction spots become resolvable at ~3 nm and that the diffraction spot intensities reach a maximum when the film is ~11 nm thick[6].

Many previously unobserved phenomena in the early stages of MgO IBAD growth are immediately apparent from RHEED analysis. A dramatic result is that the out-of-plane orientation distribution ($\Delta\omega$) starts out very broad, and then decreases during IBAD growth. It has been previously suggested that during IBAD MgO growth the grains initially nucleate with a narrow out-of-plane orientation distribution. However, it is evident that the grains nucleate with a very broad out-of-plane orientation distribution. The in-plane orientation distribution, as measured using single image analysis, narrows with film thickness. The average grain size, as well as the film roughness, increases with film thickness. It has been observed that if the IBAD MgO film grows much past 11 nm the biaxial texture degrades[6]. One of the sources of this degradation may be that MgO grain renucleation on the rough surface increases the out-of-plane orientation distribution. The resulting out-of-plane misorientation, with respect to the direction of the ion bombardment, may decrease the

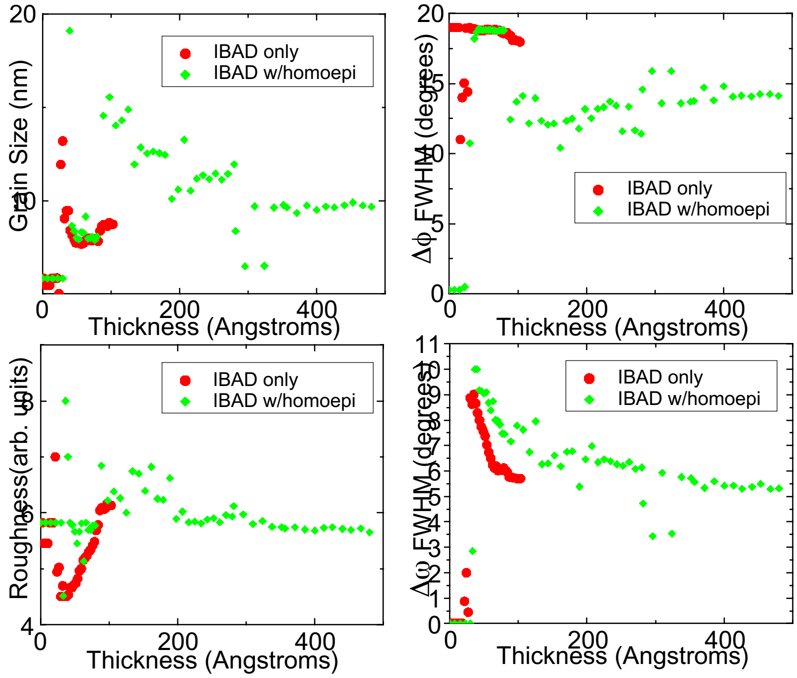


Figure 4: RHEED images from IBAD MgO growth. Film thickness increases by ~1 monolayer from image to image. Film thickness for image d is ~3 nm.

effectiveness of in-plane alignment mechanisms and result in a broader in-plane orientation distribution as well.

Figure 3 also shows the biaxial texture development during homoepitaxial growth of MgO at 600$^{o}$ C and 1 Å/s, using 15keV electrons. The grain size increases a few nanometers by increasing the substrate temperature to 600$^{o}$ C. Ion bombardment creates film defects and may even locally amorphize the IBAD MgO film. It is possible that at high temperatures the less damaged grains will grow into the more damaged grains following a mechanism similar to that proposed by Dong and Srolovitz[7]. In this growth model the more damaged, maybe even locally amorphous, grains will recrystallize and adopt the orientation of the least damaged grain. The surface energy associated with grain boundaries, which increases with temperature, may also drive grain growth. During a separate growth experiment, using the same growth conditions, we measured the in-plane orientation distribution using in-plane rocking curves. After ~11 nm of IBAD growth the in-plane orientation distribution FWHM was 12.2$^{o}$, but after an additional 500 Å of homoepitaxy the in-plane orientation distribution decreased to 9.0$^{o}$ FWHM. We note since the both the in-plane and out-of-plane orientation distributions decrease during homoepitaxial growth, previously reported X-ray analysis of biaxial texture of MgO films that have an additional homoepitaxial layer to enable measurements with a lab based X-ray source are not quantitatively representative of the

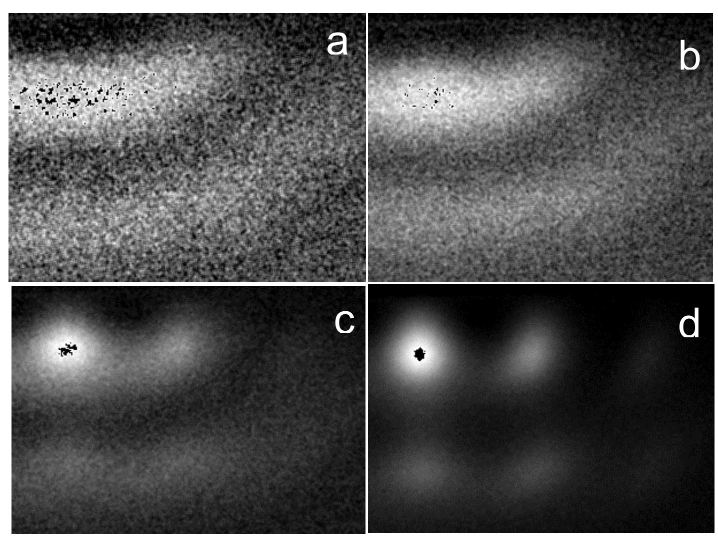


Figure 3: RHEED images from IBAD MgO growth. Film thickness increases by ~1 monolayer from image to image. Film thickness for image d is ~3 nm.

IBAD MgO film texture.

Figure 4 is a sequence of RHEED images during IBAD MgO growth. The change in film thickness between images is about 1 monolayer. The broad rings in Figures 4a and 4b are characteristic of random out-of-plane oriented polycrystalline films. These rings are consistent with MgO crystal structure and all contributions from the $\alpha$-$Si_3N_4$ substrate have been subtracted out. Subsequent images in Figures 4c and 4d show a rapid decrease in out-of-plane orientation distribution, as evidenced by the disappearance of the rings.

## CONCLUSION

We have developed a RHEED based method for quantitative biaxial texture measurement of MgO. *In situ* RHEED analysis reveals that the out of plane orientation distribution starts out very broad, and then decreases during IBAD MgO growth. Other results included evidence that the in-plane orientation distribution narrows, the grain size increases, and the film roughens as film thickness increases during IBAD MgO growth. Homoepitaxy of MgO improves the biaxial texture of the IBAD layer, making X-ray measurements of IBAD films with an additional homoepitaxial layer not quantitatively representative of the IBAD layer. The systematic offsets between RHEED analysis and X-ray measurements of biaxial texture, coupled with evidence that biaxial texture improves with increasing film thickness, indicates that RHEED is a superior technique for probing surface biaxial texture. This technique provides novel information about the biaxial texture development and will facilitate rapid investigation of biaxial texturing mechanisms and biaxial texture optimization.


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## REFERENCES


1. R.T. Brewer, J.W. Hartman, and H.A. Atwater, Mat. Res. Soc. Symp. Proc. **585**, 75 (2000).
2. W.J. Lin, T.Y. Tseng, H.B. Lu, S.L. Tu, S.J. Yang, and I.N. Lin, J. Appl. Phys., **77**, 6466 (1995).
3. N. Wakiya, K. Kuroyanagi, Y. Xuan, K. Shinozaki, and N. Mizutani, Thin Solid Films, **357**, 166 (1999).
4. R.A. McKee, F.J. Walker, and M.F. Chisholm, Phys. Rev. Lett., **81**, 3014 (1998).
5. C.P. Wang, K.B. Do, M.R. Beasley, T.H. Geballe, and R.H. Hammond, Appl. Phys. Lett. **71**, 2955 (1997).
6. C.P. Wang, Ph.D. Thesis, Stanford University, (1999).
7. L. Dong and D.J. Srolovitz, J. Appl. Phys. **84**, 5261 (1998).